Elimination–Rearrangement in β -Functionalised Silanes—the Direction of the Rearrangement and its Scope

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A new eliminative rearrangement of β -silyl carbanions requires phenyl on carbon α - to silicon when the conjugate acid has a pK_a (DMSO) in the range 12–30; rearrangement involves silicon and not phenyl migration.

In an earlier communication,¹ we reported that when silanes 1 were treated with strongly basic but silicophilic nucleophiles such as *tert*-butoxide, competition between silicophilic and protophilic eliminations was observed (Scheme 1).



When, however, a strong but poorly silicophilic base, such as LDA, was used, the reaction took a third course, via 2 to give² the rearranged alkene 3. The latter process was observed with R = Ph and when Z was a carbanion-stabilising leaving group such as SPh, SO₂Ph or CN. The rearrangement occurs via the β -carbanion 2 for Z = CN and SO₂Ph, but formation of 3 from 1 is concerted when Z = SPh.

These studies left three significant questions unanswered.

(*i*) Is the formation of **3a** from **1a** by rearrangement via **2** $[pK_a^{(DMSO)}$ of EtSO₂Ph = 31.0³] or by protophilic elimination as for **1a** to **4a**?

(*ii*) In the formation of **3b** from **1b**, is rearrangement by migration of the trimethylsilyl group or of the phenyl group?

(iii) Are there limits to the observed rearrangement?

We now have answers to these questions as follows.

(i) Silane 1 (R = D; Z = SO₂Ph)¹ was treated with a three molar excess of LDA in THF. After reflux (3 h) and work-up, the solvent and volatiles including trimethyl(vinyl)silane were distilled off and treated at -30 °C with an excess of toluene-4-sulfenyl chloride. The silyl sulfide 5, but none of the isomer 6, was detected by ¹H NMR spectroscopy, demonstrating that the α -phenyl group is required for rearrangement.

(ii) Our earlier studies did not distinguish between phenyl

 $p - \text{MeC}_{6}\text{H}_{4}\text{S} \underbrace{\downarrow_{D}}_{CH_{2}\text{CI}} p - \text{MeC}_{6}\text{H}_{4}\text{S} \underbrace{\downarrow_{H}}_{H}^{SiMe_{3}}$ $cH_{2}\text{CI} CHDCI$ 5 6

and trimethylsilyl migration. Treatment of 7^1 and 8 [obtained by quenching the anion 2b (Z = SO₂Ph) with D₂O] separately with LDA in THF gave E/Z mixtures of styrenes 9 and 10 respectively (Scheme 2). These results exclude phenyl migration.



(iii) As already mentioned, 1a ($Z = SO_2Ph$) undergoes protophilic elimination rather than rearrangement; treatment of both 11 and 12 obtained as shown in Scheme 3, with LDA– THF under forcing conditions (reflux, 24 h) gave no products and they were recovered in high yields. These much more acidic substrates [$pK_a^{(DMSO)}$ PhSO₂Ph 23.4⁴; $pK_a^{(DMSO)}$ (PhSO₂)₂CH₂ = 12.2³] are presumably completely converted into their β anions which are too weakly reactive to rearrange without an α -phenyl group present, but the protophilic pathway is thereby inhibited.



Scheme 3 Reagents: i, PhSO₂CH₂Ph-LDA-THF; ii, (PhSO₂)₂CH₂-EtONa-EtOH

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